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A Highly Stable Organic Radical Cation

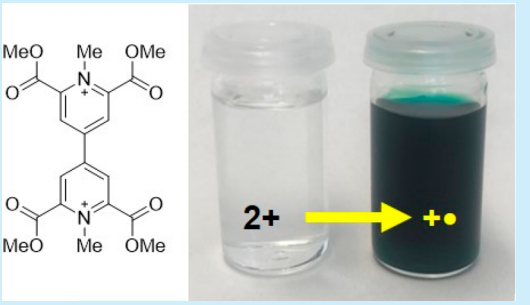
Mathilde Berville,[†] Jimmy Richard,[†] Monika Stolar,[‡] Sylvie Choua,[†] Nolwenn Le Breton,[†] Christophe Gourlaouen,[†] Corinne Boudon,[†] Laurent Ruhlmann,[†] Thomas Baumgartner,[‡] Jennifer A. Wytko,*[,†] and Jean Weiss*[,†]

[†]Institut de Chimie de Strasbourg, UMR 7177 Université de Strasbourg-CNRS, Institut LeBel, 4 rue Blaise Pascal, 67008 Strasbourg, France

[‡]Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario M3J 1P3, Canada

Supporting Information

ABSTRACT: Functionalization of a methylviologen with four methyl ester substituents significantly facilitates the first two reduction steps. The easily generated radical cation showed markedly improved air stability compared to the parent methylviologen, making this derivative of interest in organic electronic applications.

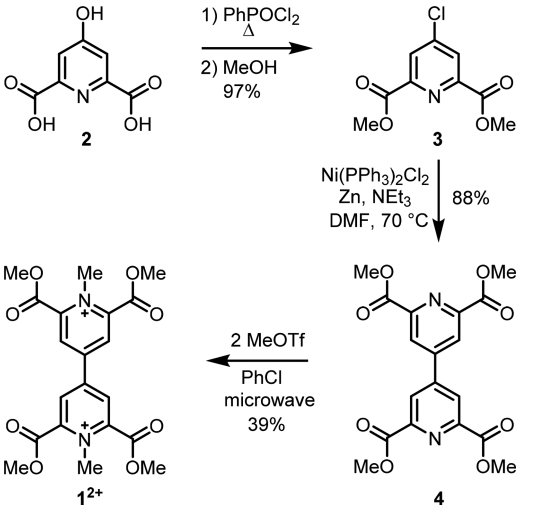


Among the strong, organic-based electron acceptors, quaternized derivatives of 4,4′-bipyridine, also known as viologens, are promising candidates for applications in organic electronics,[1] molecular machines,[2] and as functional materials.[3] Interest in this family of acceptors stems from their simple preparation, stability, and three, distinctly colored, redox states.[4] Stable organic acceptors for which the first reduction potential is near 0 V, or even positive, are highly desirable for practical applications.[2] Tuning the potential of viologen derivatives is commonly achieved by changing the N-substituent (either alkyl or aryl) or the counteranions.[5,6] Another more effective strategy that significantly facilitates the first reduction compared to that of methyl viologen (MV^{2+}) utilizes the introduction of main-group element[7−11] or carbon[12] bridges between the pyridyl moieties of the viologen framework. Few other reports describe the functionalization of the viologen's carbon skeleton with electron-withdrawing groups as a method to alter its electronic properties.[13]

Herein, we describe two remarkable features of a viologen ($\mathbf{1}^{2+}$) bearing methyl ester groups at the 2,2′,6,6′ positions. Not only do these four electron-withdrawing groups significantly facilitate both reduction potentials but they also stabilize the radical cation in organic solution, even in the presence of oxygen. Although viologen radical cations can be stabilized as dimers under argon at low temperature[4] or in host−guest systems,[14] and air-stable viologen radical cations encapsulated in catenanes have been reported by Stoddart,[15] there are no other examples of simple viologen derivatives in a stable radical-cation state.

The tetraester viologen $\mathbf{1}^{2+}$ was synthesized in three steps starting from chelidamic acid[16,17] **2** (Scheme 1), which was transformed to the methyl ester of the chloropyridine derivative **3** by subsequent treatment with $PhPOCl_2$ and MeOH.[18] After optimization of the previously reported coupling conditions by Oda et al.,[19] chloropyridine **3** underwent clean homocoupling that afforded bipyridine **4** in 88% yield. Quaternization of the nitrogen atoms of the bipyridine required harsh conditions, indicating the weak nucleophilic character of the pyridine nitrogen atoms. Treatment of **4** with methyl triflate (MeOTf) under microwave irradiation afforded viologen $\mathbf{1}^{2+}$ as its triflate salt in 39% yield.

Scheme 1. Synthesis of the Tetraester Viologen $\mathbf{1}^{2+}$



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Single crystals of the dicationic species were obtained by slow diffusion of Et_2O in MeCN. In the solid-state structure[20] of $\mathbf{1}^{2+}$ (Figure 1), the bipyridinium rings are twisted with a 32°

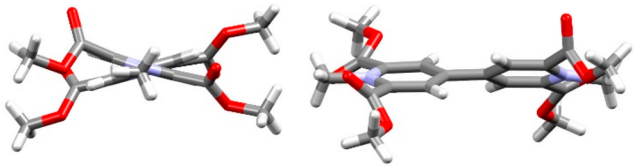

Figure 1. Side views of the viologen $\mathbf{1}^{2+}$ in the solid state. Triflate anions and solvent molecules have been omitted for clarity.

dihedral angle that is closer to the 36° twist of 1,1′-diphenylviologen[21] than to the nearly coplanar structures observed for most 1,1-dialkylviologen dications. The structure of $\mathbf{1}^{2+}$ also shows the possible formation of intramolecular hydrogen bonds between the ester groups and the N-methyl substituents (2.1−2.5 Å) or the pyridine protons (~2.4 Å) (see Supporting Information).

The redox properties of $\mathbf{1}^{2+}$ were investigated by electrochemical methods. Cyclic voltammetry (CV) on a glassy carbon electrode in CH_3CN solutions with tetrabutylammonium hexafluorophosphate ($TBAPF_6$; 0.1 M) as supporting electrolyte showed three reversible reductions (Figure 2a). The first two one-electron reductions at −0.27 and −0.50 V versus Fc^+/Fc are, respectively, attributed to the formation of the radical cation $\mathbf{1}^{\bullet+}$ and the neutral $\mathbf{1}^0$. The third reduction detected from the CV at −1.90 V versus Fc^+/Fc is a two-electron event that generates $\mathbf{1}^{2-}$. This reduction was almost absent in rotating disk electrode experiments (Figure 2b), suggesting that the neutral form ($\mathbf{1}^0$) undergoes a relatively slow chemical reaction once formed. It is also possible that the generated $\mathbf{1}^{2-}$ species is sparingly soluble in the 0.1 M $TBAPF_6$ CH_3CN medium. Controlled-potential coulometry at −0.37 and at −0.60 V versus Fc^+/Fc resulted in the respective exchange of 0.97 and 1.85 electrons per molecule of compound **1**.

The first two reductions of $\mathbf{1}^{2+}$ are shifted by +560 and +740 mV, respectively, compared to those of MV^{2+} ($E_{red1,1/2}$ = −0.83 V and $E_{red2,1/2}$ = −1.24 V vs Fc^+/Fc) under the same experimental conditions. The significantly less cathodic values of these potentials are attributed to the presence of the four electron-withdrawing ester groups. When the same ester groups are appended to an aryl ring at the quaternized nitrogen atoms of a viologen, the electronic effects are less pronounced[6] than in $\mathbf{1}^{2+}$. Hence, conjugation effects also play a role in tuning the redox properties, as supported by the small contribution of the ester group in the density functional theory (DFT)-generated singly occupied molecular orbital (SOMO) (Figure 3 and Supporting Information).

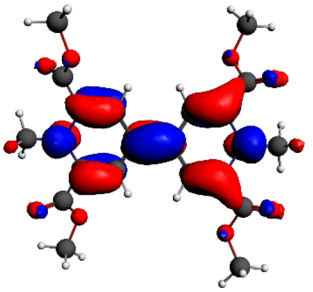

Figure 3. ADF view drawing of the Kohn−Sham SOMO of the radical cation $\mathbf{1}^{\bullet+}$.

The colorless divalent viologen $\mathbf{1}^{2+}$ mainly absorbs at 278 nm (Figure 4, blue spectrum). Upon one-electron reduction, this absorbance decreases in intensity, while new absorption bands grow at 334, 417, 769, and 852 nm (shoulder) for the green radical cation $\mathbf{1}^{\bullet+}$ (Figure 4, green spectrum and Supporting Information). The absence of absorption bands in the near-infrared (NIR) indicates that π-dimers do not form[4] in solution at 1×10^{-3} M and suggests that the radical cation is stabilized only by the four electron-withdrawing ester groups. We attribute the broadness of the absorption centered at 769 nm to the coexistence of several possible conformations of the ester groups, as seen in DFT calculations, or to vibrational states.[22] The second reduction generates a red, neutral viologen species $\mathbf{1}^0$ that absorbs at 492 nm (Figure 4, red spectrum). Aside from indicating the absence of π-dimer formation, an interesting feature of the UV−vis−NIR monitoring of the three species $\mathbf{1}^{2+}$, $\mathbf{1}^{\bullet+}$, and $\mathbf{1}^0$ is their individually addressable character and readability at specific wavelengths. Reversible changes of the absorptions at 278, 417,

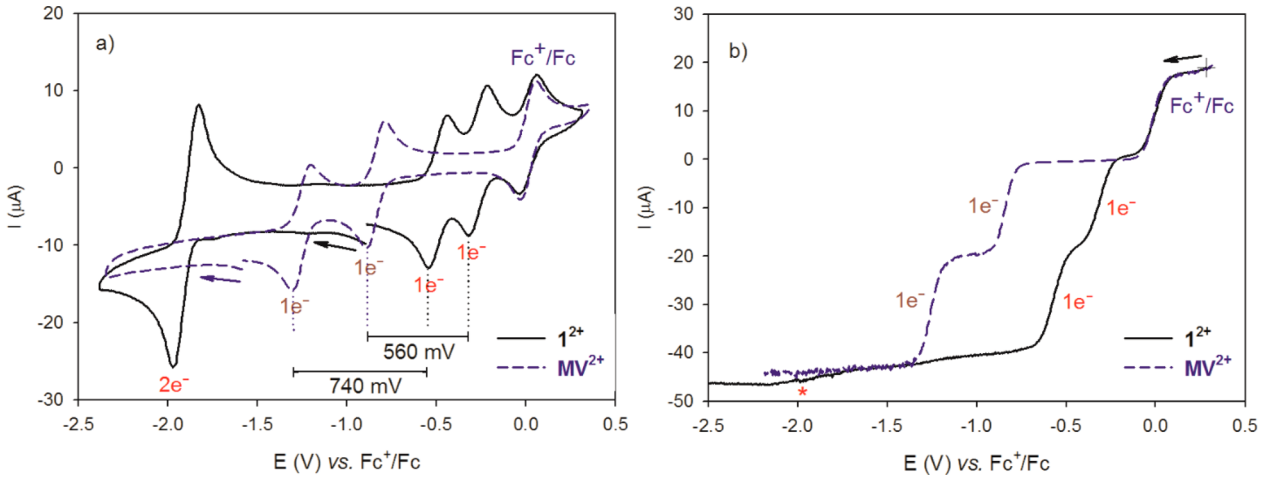

Figure 2. CV (a) and rotating disk electrode voltammetry (b) of $\mathbf{1}^{2+}$ and $\mathbf{MV}^{2+}$ in CH_3CN + 0.1 M $TBAPF_6$: working electrode = glassy carbon, pseudoreference = Pt, counter electrode = Pt, internal reference = Fc. (a) ν = 0.1 V/s; (b) ν = 0.02 V/s, rotation: 1000 rpm.

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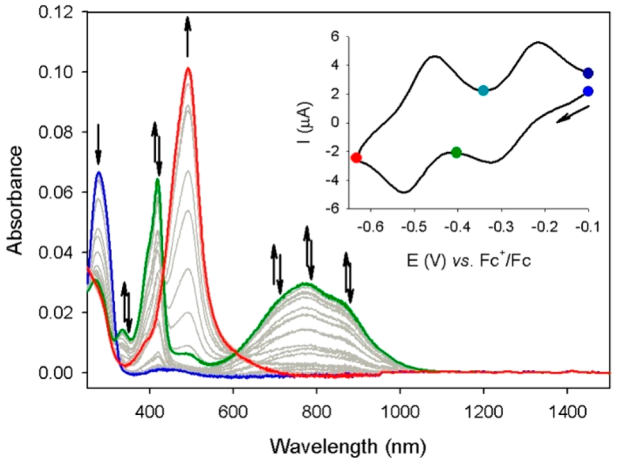

Figure 4. UV−Vis−NIR monitoring of the reduction of $\mathbf{1}^{2+}$. (inset) Corresponding CV at scan rate of 0.01 V s^{-1}. Solution ($c = 1 \times 10^{-3}$ M) of $\mathbf{1}^{2+}$ in CH_3CN + 0.1 M $TBAPF_6$ recorded with an optically transparent thin-layer (0.2 mm) electrochemical cell equipped with an Au mini-grid WE and CaF_2 optical windows, reference AgCl/Ag.

492, and 769 nm over several reduction−oxidation cycles confirmed the reversibility of the redox interconversion features of the three redox states (see Supporting Information).

Electron paramagnetic resonance (EPR) studies confirmed the paramagnetic, radical character of $\mathbf{1}^{\bullet+}$. The reaction of $\mathbf{1}^{2+}$ with 1 equiv of ascorbic acid yielded a well-resolved EPR spectrum (Figure 5) centered at $g = 2.0032$ corresponding to

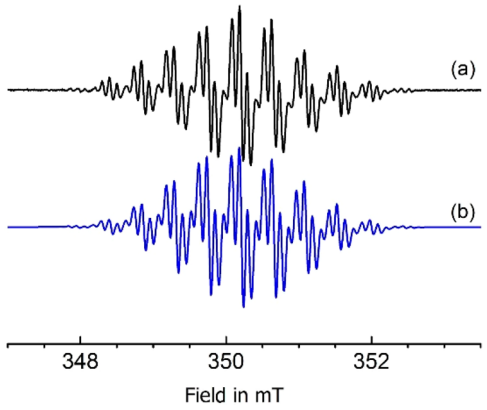

Figure 5. X-band EPR spectrum of $\mathbf{1}^{\bullet+}$ (a) in CH_3CN at 10^{-3} M at room temperature; (b) simulated spectrum.

two sets of four and six equivalent protons ($A_1(^1H) = 0.11$ mT, $A_2(^1H) = 0.43$ mT), respectively, and one set with two equivalent nitrogen atoms ($A_1(^{14}N) = 0.45$ mT). The same spectrum was obtained by electrolysis. The colorless solution turned green upon one-electron reduction to generate the radical cation $\mathbf{1}^{\bullet+}$. After the second reduction, the solution turned red, and the intensity of the EPR spectrum decreased gradually to give the silent neutral species $\mathbf{1}^0$.

The air stability of the radical cation $\mathbf{1}^{\bullet+}$ over time was also investigated by EPR (Figure 6). After the radical cation was generated by coulometry in MeCN, samples of the solution of $\mathbf{1}^{\bullet+}$ were transferred to EPR tubes purged with argon or open to air. The argon sample was stable for more than 40 h. Even after three months, the intensity of the EPR spectrum of the same solution remained constant. For samples under air, the

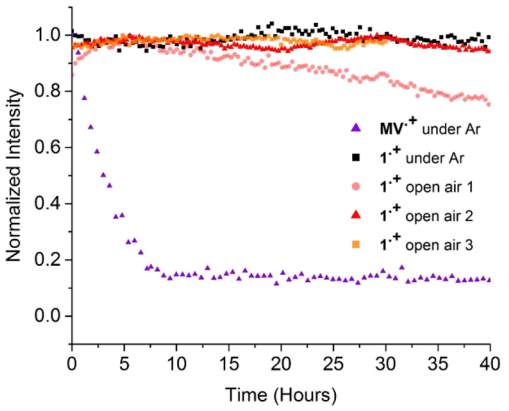

Figure 6. Double integrated EPR spectrum of $\mathbf{1}^{\bullet+}$ and $MV^{\bullet+}$ in CH_3CN at 1×10^{-3} M at room temperature under Ar and open to air.

intensity of the EPR signal of $\mathbf{1}^{\bullet+}$ remained relatively stable over 40 h in two cases. In the third case (Figure 6, $\mathbf{1}^{\bullet+}$ open air 3), the intensity of the EPR signal increased initially over the first 5 h and then decreased by ~25% after 40 h. We assign the initial increase to the presence of some diamagnetic dimeric species $(\mathbf{1}^{\bullet+})_2$ that dissociate into paramagnetic $\mathbf{1}^{\bullet+}$ monomers within the first few hours. The presence of oxygen in the samples exposed to air was confirmed by a broad EPR signal (see Supporting Information). Under the same experimental conditions, the $MV^{\bullet+}$ reference compound was considerably less stable under argon, as demonstrated by the rapid decay[23] of the EPR signal within a few hours (Figure 6). In the presence of air, $MV^{\bullet+}$ was very unstable, and no EPR signal was observed. Together, these data confirmed the high stability of $\mathbf{1}^{\bullet+}$.

Despite the stability of the radical cation, we were unable to grow single crystals of sufficient quality for X-ray diffraction. Thus, optimizations of the geometries of $\mathbf{1}^{2+}$ and $\mathbf{1}^{\bullet+}$ were performed without any symmetry restriction. For the dication $\mathbf{1}^{2+}$, the twist between the pyridinium rings was reproduced (33° vs 32°), and the accord between experimental and calculated geometry remained quite satisfactory. A large highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO) energy gap was calculated (4.60 eV) for $\mathbf{1}^{2+}$, but the LUMO was stabilized by 0.7 eV compared to MV^{2+}. These calculations corroborate with the electrochemical data.

When the dication $\mathbf{1}^{2+}$ is reduced to $\mathbf{1}^{\bullet+}$, the optimized geometrical parameters provide a more planar structure with a value of dihedral angle of 15°. This twist is higher than the 6° and 11° observed in the two independent molecules of the X-ray structure of $MV^{\bullet+}$.[24] Comparison of these data suggests less electronic delocalization in $\mathbf{1}^{\bullet+}$ than in $MV^{\bullet+}$. The calculated ^1H and ^{14}N isotropic constants (see Supporting Information) are in close agreement with the experimental values. As shown by the SOMO illustrated in Figure 3, the unpaired electron is essentially localized on the pyridine rings, on both N-methyl groups, and only slightly on the tetraester substituents. This observation supports the stabilizing effect of the four electron-withdrawing ester groups on the radical cation.

In conclusion, the tetraester derivative of methylviologen is a strong electron acceptor that converts easily and reversibly into its radical cation species. Because of the electron-attracting effect of the ester groups, the radical species is stable for months under argon and for hours in the presence of oxygen.

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These features are of great interest from the perspective of air-operating electrochromic devices and molecular switches. Isolation and investigations of $\mathbf{1}^{\bullet+}$ as a solid material are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03579.

Experimental procedures, spectro-electrochemical and EPR spectra, hyperfine coupling constants, calculated molecular orbitals, X-ray crystal data (PDF)

Accession Codes

CCDC 1846774 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: jweiss@unistra.fr. (J.A.W.)
*E-mail: jweiss@unistra.fr. (J.W.)

ORCID

Thomas Baumgartner: 0000-0001-8066-0559
Jennifer A. Wytko: 0000-0001-5370-4253

Author Contributions

All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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